Science Front Publishers *Journal for Foundations and Applications of Physics*, **vol. 4, No. 2 (2017)**
(sciencefront.org) **ISSN 2394-3688**

The contact angle for spherical droplet in rough and homogeneous cavity with arc generatrix

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(Received 10 July 2017, Accepted 13 August 2017, Published 02 September 2017)

Abstract

The contact angle for spherical droplet in rough and homogeneous cavity with arc generatix is studied. The solid-liquid-vapor system is separated into six portions. A generalized Wenzel equation for the contact angle considering the line tension effects is developed for the three-phase system. Under certain hypotheses, this generalized Wenzel equation is the same as the classical Wenzel equation.

***Keywords*:** Contact angle; Wenzel equation; Line tension; Cavity; Surface tension

1. Introduction

The contact angle of droplet on solid is the important characteristic of wetting. For the wetting of solid surface by a liquid, Young firstly presented the contact angle equation [1]

$$\cos\theta_Y = \frac{\sigma_{SG} - \sigma_{SL}}{\sigma_{LG}} \tag{1}$$

where θ_Y is the contact angle, σ represents the interfacial tension. S, L and G symbolize solid, liquid, and vapor phase, respectively.

If a solid surface is not smooth, the equation(1) is not valid. For the rough solid surface, contact angle is described by the Wenzel equation [2]

$$\cos\theta = r_S \cos\theta_Y \tag{2}$$

where θ is the contact angle, r_S is the surface roughness factor.

Equations (1) and (2) ignore the three-phase molecular interactions at the contact line. The contact line was firstly postulated by Gibbs [3]. He proposed that the contact line has the considerably influence in the three-phase system. Gibbs thinks that the line tension results from the excess energy located at the three-phase junction. From then on, many experimental and theoretical studies were made with regard to the line tension[4-6]. Allowing for the line tension effects, for rough solid substrates, a modified Young equation was presented by Rusanov[7]

$$\cos\theta = r_S \cos\theta_Y - \left[\frac{r_L \kappa}{R_L} + \frac{\partial (r_L \kappa)}{\partial R_L}\right]\frac{|\cos\varphi|}{\sigma_{LG}} \tag{3}$$

where φ is the angle between the substrate surface and the local osculating plane of the three-phase contact line, R_L represents the radius of the three-phase contact line, κ is the corresponding line tension, r_L is the line roughness factor. The r_S and r_L defined as

$$r_S = A_{SL}^{'} / A_{SL},\ r_L = L^{'} / L \tag{4}$$

where A and L are the apparent value of the surface and the length of the three-phase contact line, and $A^{'}$ and $L^{'}$ are their true value.

Equation (3) corresponds to a very particular choice of the dividing surface between the liquid phase and the vapor phase. For spherical droplet in a smooth and homogeneous conical cavity surface rotated by arc, taking the line tension effects into consideration, on the basis of the method of Gibbs's dividing surfaces, a generalized Young equation was presented by Ai-Jun Hu [8]

$$\cos\theta = \cos\theta_Y - \frac{k}{\sigma_{LG} R_L}\sqrt{1-\left(\frac{R_L}{R_0}-1\right)^2} - \frac{1}{\sigma_{LG}}\sqrt{1-\left(\frac{R_L}{R_0}-1\right)^2}\cdot\left[\frac{dk}{dR_L}\right] \tag{5}$$

where R_0 is the radius of the arc.

Equation (5) ignore the surface roughness factor and the line roughness factor effects. In this study, considering the line tension effects, wetting of spherical droplet in rough and homogeneous cavity surface rotated by arc is studied. A generalized Wenzel equation for the contact angle is obtained according to the methods of dividing surfaces of Gibbs based on thermodynamics.

2. Calculation of the free energy of the solid-liquid-vapor system

The wetting of droplet in the rough and homogeneous cavity surface rotated by arc around the z axis was illustrated in Figure 1. R_0 is the radius of the arc. β denotes the angle between the substrate surfaces tangent and the principal plane of the three-phase contact line. α denotes the angle between the liquid droplet surface tangent and the local principal plane of the contact line. In this paper, we neglected the droplet gravity. So, the equilibrium shape of droplet above the principal plane of the three-phase contact line in the rough and homogeneous cavity surface rotated by arc around the z axis bears the shape of a spherical part.

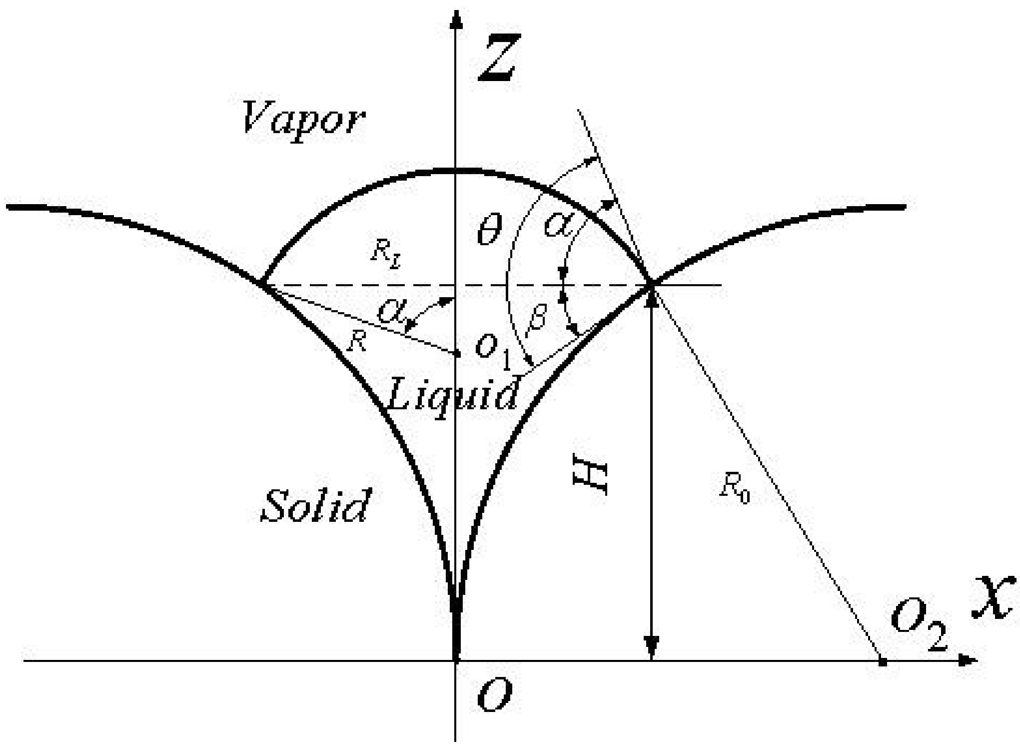

Figure 1 Wetting of a spherical droplet in rough and homogeneous cavity surface rotated by arc around z axis

On the basis of the method of Gibbs's dividing surface[3], the solid-liquid-vapor system is separated into the following portions, liquid phase, vapor phase, solid-liquid interface, solid-vapor interface, liquid-vapor interface, and the three-phase contact line. There is the Helmholtz free energy F of the three phase system

$$F = F_L + F_G + F_{SL} + F_{SG} + F_{LG} + F_{SLG} \tag{6}$$

where F_L, F_G, F_{SL}, F_{SG}, F_{LG} and F_{SLG} are the free energies of six portions, respectively. The free energies of six portions is[9]

$$F_L = -p_L V_L + \mu_L N_L \tag{7}$$

$$F_G = -p_G V_G + \mu_G N_G \tag{8}$$

$$F_{SL} = \sigma_{SL} A_{SL} + \mu_{SL} N_{SL} \tag{9}$$

$$F_{SG} = \sigma_{SG} A_{SG} + \mu_{SG} N_{SG} \tag{10}$$

$$F_{LG} = \sigma_{LG} A_{LG} + \mu_{LG} N_{LG} \tag{11}$$

$$F_{SLG} = k L_{SLG} + \mu_{SLG} N_{SLG} \tag{12}$$

where p, V, μ indicate the pressure, the volume, the chemical potential of the phase, N is the corresponding mole number of molecule, σ indicates the surface tension, A denotes the surface area, k indicates the line tension, and L indicates the length of the triple phase contact line. Subscripts S , L and G indicate solid, liquid, and vapor phase, respectively.

The volume V_L of liquid phase is elicited, according to the illustration shown in Figure 1

$$V_L = \int_0^H \pi x^2 dz + \frac{\pi}{3} R^3 (2+\cos\alpha)(1-\cos\alpha)^2 \tag{13}$$

where R is the radius of the spherical drop. H is the height from local principal plane of contact line to the bottom of cone.

The whole volume V_t of the liquid phase and vapor phase is

$$V_t = V_L + V_G \tag{14}$$

The liquid-vapor interface surface area A_{LG} is

$$A_{LG} = 2\pi R^2 (1-\cos\alpha) \tag{15}$$

The solid-liquid interface apparent surface area A_{SLa} is given by

$$A_{SLa} = \int_0^H 2\pi x \sqrt{1+(\frac{dx}{dz})^2}\, dz \tag{16}$$

The true value of the solid-liquid interface surface area A_{SL} is

$$A_{SL} = r_S \int_0^H 2\pi x \sqrt{1+(\frac{dx}{dz})^2}\, dz \tag{17}$$

The whole surface area A_t of the solid-liquid and solid-vapor interfaces is

$$A_t = A_{SL} + A_{SG} \tag{18}$$

The apparent value and true value of the length of the three-phase contact line can be given by

$$L_{SLGa} = 2\pi R \sin\alpha \tag{19}$$

and

$$L_{SLG} = 2\pi R r_L \sin\alpha \tag{20}$$

respectively.

Based on the previous formulae, we have the free energy of the three phase system

$$F_L = -p_L \left[\int_0^H \pi x^2 dz + \frac{\pi}{3} R^3 (2+\cos\alpha)(1-\cos\alpha)^2 \right] + \mu_L N_L \tag{21}$$

$$F_G = -p_G \left\{ V_t - \left[\int_0^H \pi x^2 dz + \frac{\pi}{3} R^3 (2+\cos\alpha)(1-\cos\alpha)^2 \right] \right\} + \mu_G N_G \tag{22}$$

$$F_{SL} = \sigma_{SL} r_S \left[\int_0^H 2\pi x \sqrt{1+(\frac{dx}{dz})^2}\, dz \right] + \mu_{SL} N_{SL} \tag{23}$$

$$F_{SG} = \sigma_{SG} \left\{ A_t - r_S \left[\int_0^H 2\pi x \sqrt{1+(\frac{dx}{dz})^2}\, dz \right] \right\} + \mu_{SG} N_{SG} \tag{24}$$

$$F_{LG} = \sigma_{LG} \cdot 2\pi R^2 (1-\cos\alpha) + \mu_{LG} N_{LG} \tag{25}$$

$$F_{SLG} = 2\pi k R r_L \sin\alpha + \mu_{SLG} N_{SLG} \tag{26}$$

Putting the above formulae into Eq.(6), the whole free energy of the system can be described as following formula.

$$\begin{aligned} F = &-(p_L - p_G)\left[\int_0^H \pi x^2 dz + \frac{\pi}{3} R^3 (2+\cos\alpha)(1-\cos\alpha)^2\right] \\ &- p_G V_t + \sigma_{LG} \cdot 2\pi R^2 (1-\cos\alpha) + (\sigma_{SL} - \sigma_{SG}) \cdot r_S \int_0^H 2\pi x \sqrt{1+(\frac{dx}{dz})^2} dz \\ &+ \sigma_{SG} A_t + 2\pi k r_L R \sin\alpha + \mu_L N_L + \mu_G N_G + \mu_{LG} N_{LG} + \mu_{SL} N_{SL} + \mu_{SG} N_{SG} + \mu_{SLG} N_{SLG} \end{aligned} \tag{27}$$

3. Derivation of generalized Young equation for the contact angle

The grand potential Ω of the solid, liquid, and vapor three phase system is

$$\Omega = F - \sum_i \mu_i N_i \tag{28}$$

where i indicates the amount of part of the system.

Substituting Eq. (27) into Eq. (28) , the following expression is obtained

$$\begin{aligned} \Omega = &-(p_L - p_G)\left[\int_0^H \pi x^2 dz + \frac{\pi}{3} R^3 (2+\cos\alpha)(1-\cos\alpha)^2\right] \\ &- p_G V_t + \sigma_{LG} \cdot 2\pi R^2 (1-\cos\alpha) + (\sigma_{SL} - \sigma_{SG}) \cdot r_S \int_0^H 2\pi x \sqrt{1+(\frac{dx}{dz})^2} dz \\ &+ \sigma_{SG} A_t + 2\pi k r_L R \sin\alpha \end{aligned} \tag{29}$$

We suppose the actual physical characteristics of the three phase system are fixed. Thus, the grand thermodynamic potential Ω, σ_{SL} and σ_{SG} don't depend on the notional variation of the radius R of the droplet, the following conditions can be obtained [9,10]

$$\left[\frac{d\Omega}{dR}\right] = 0, \quad \left[\frac{d\sigma_{SL}}{dR}\right] = 0, \quad \left[\frac{d\sigma_{SG}}{dR}\right] = 0 \tag{30}$$

Substituting Eq.(29) into Eq.(30), we arrived at the following equation

$$\begin{aligned} &-(p_L - p_G) \cdot \left[\frac{dV_L}{dR}\right] + \left[\frac{d\sigma_{LG}}{dR}\right] \cdot A_{LG} + \sigma_{LG} \cdot \left[\frac{dA_{LG}}{dR}\right] + (\sigma_{SL} - \sigma_{SG}) \cdot \left[\frac{dA_{SL}}{dR}\right] \\ &+ \left[\frac{dk}{dR}\right] \cdot L_{SLG} + k \cdot \left[\frac{dL_{SLG}}{dR}\right] = 0 \end{aligned} \tag{31}$$

The dividing surface of liquid-vapor interface of a free spherical liquid droplet is concentric. Thus, we have the following expressions

$$\begin{aligned} &H - R\cos\alpha = \overline{oo_1} = const \\ &H = \sqrt{R_0^2 - (R\sin\alpha - R_0)^2} \end{aligned} \tag{32}$$

$$R_L = R\sin\alpha \tag{33}$$

and

$$\frac{d\alpha}{dR}=\frac{\sin\alpha\cdot(R\sin\alpha-R_0)+\cos\alpha\cdot\sqrt{R_0^2-(R\sin\alpha-R_0)^2}}{R\sin\alpha\cdot\sqrt{R_0^2-(R\sin\alpha-R_0)^2}-R\cos\alpha\cdot(R\sin\alpha-R_0)} \tag{34}$$

$$\frac{dH}{dR}=\frac{-(R\sin\alpha-R_0)}{\sin\alpha\cdot\sqrt{R_0^2-(R\sin\alpha-R_0)^2}-\cos\alpha\cdot(R\sin\alpha-R_0)} \tag{35}$$

$$\frac{dR_L}{dR}=\frac{\cos\beta}{\sin(\alpha+\beta)} \tag{36}$$

According to Eqs. (32-36), the following results are obtained

$$\left[\frac{dV_L}{dR}\right]=2\pi R^2(1-\cos\alpha) \tag{37}$$

$$\left[\frac{dA_{LG}}{dR}\right]=4\pi R(1-\cos\alpha)+\frac{2\pi R\sin\alpha\cdot\cos(\alpha+\beta)}{\sin(\alpha+\beta)} \tag{38}$$

$$\left[\frac{dA_{SL}}{dR}\right]=\frac{2\pi r_S R\sin\alpha}{\sin(\alpha+\beta)} \tag{39}$$

$$\left[\frac{dL_{SLG}}{dR}\right]=\frac{2\pi r_L\cos\beta}{\sin(\alpha+\beta)} \tag{40}$$

According to the Laplace' equation [17, 18] of a free spherical liquid drop in vapor, the following equation is obtained

$$p_L-p_G=\frac{2\sigma_{LG}}{R}+\left[\frac{d\sigma_{LG}}{dR}\right] \tag{41}$$

Based on the geometrical relations illustrated in Figure 1, the following expression is obtained

$$\cos\beta=\frac{\sqrt{R_0^2-(R\sin\alpha-R_0)^2}}{R_0} \tag{42}$$

Now substituting Eqs.(32-41) into Eq.(31) and using Eq.(42), we have

$$\cos\theta=r_S\frac{\sigma_{SG}-\sigma_{SL}}{\sigma_{LG}}-\frac{r_Lk\cos\beta}{\sigma_{LG}R\sin\alpha}-\frac{\sin\theta}{\sigma_{LG}}\cdot\left[\frac{d(r_Lk)}{dR}\right] \tag{43}$$

Noticing $\theta=\alpha+\beta$, using Young's equation Eq.(1) , Eq.(36), Eq.(43) can be rewritten as

$$\cos\theta=r_S\cos\theta_Y-\frac{r_Lk}{\sigma_{LG}R_L}\sqrt{1-\left(\frac{R_L}{R_0}-1\right)^2}-\frac{1}{\sigma_{LG}}\sqrt{1-\left(\frac{R_L}{R_0}-1\right)^2}\cdot\left[\frac{d(r_Lk)}{dR_L}\right] \tag{44}$$

Eq.(44) is the generalized Wenzel equation for spherical nanodroplet in rough and homogeneous cavity with arc generatix.

When $R_S=1$ and $R_L=1$, Eq.(44) is the same as the Eq.(5). If the line tension is assumed to be negligible, Eq. (44) changes to the classical Wenzel equation (2).

4. Conclusion

We have studied the wetting of spherical nanodroplet in rough and homogeneous cavity with arc generatix based on thermodynamics utilizing the method of Gibbs's dividing surface. We propose a generalized Wenzel equation for the contact angle of a spherical nanodroplet in the conical cavity surface revolved by arc, taking the line tension effects into consideration, on the basis of the method of Gibbs's dividing surfaces. Based on given conditions, this generalized Wenzel equation changes to the classical Wenzel equation.

Acknowledgments

This work was supported the Project of Natural Science of the Education of Henan Province (Grant No. 2011A460006), and the Doctor Research Foundation of Henan Polytechnic University (Grant No. B2009-16).

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